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(54) Title: PROCESS FOR PREPARING COBALT CATALYSTS ON TITANIA SUPPORT

(57) Abstract: Catalysts comprising cobalt on a *titania* support are produced by mixing together particles of a solid titania support and an aqueous solution of cobalt ammine carbonate, and heating to an elevated temperature sufficient to effect decomposition of the cobalt ammine carbonate and precipitation of a cobalt species onto said support. The catalysts are useful in hydrogenation and Fischer-Tropsch reactions.

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PROCESS FOR PREPARING COBALT CATALYSTS ON TITANIA SUPPORT

Cobalt catalysts

This invention relates to cobalt catalysts comprising cobalt supported on a solid titania support and in particular to a method for manufacturing such catalysts.

Catalysts comprising cobalt on a support such as silica or alumina are known in the art for hydrogenation reactions, e.g. for the hydrogenation of chemicals such as aldehydes and nitriles and for the preparation of hydrocarbons from synthesis gas via the Fischer-Tropsch reaction.

WO-A-96/04072 discloses a cobalt on transition alumina catalyst containing between 3 and 40% by weight of cobalt and having a cobalt surface area greater than 30 m²/g cobalt.

EP-A-0013275 discloses coprecipitated cobalt-silica hydrogenation catalysts prepared by adding an alkaline precipitating agent to a heated mixture containing cobalt cations, silicate anions and solid porous carrier particles under agitation thereby to precipitate the cobalt and silicate ions onto the solid support particles.

WO-A-02/089978 describes a catalyst for use in the Fischer-Tropsch process, comprising at least one metal selected from the group consisting of nickel, cobalt, iron, ruthenium, osmium, platinum, palladium, iridium, rhenium, molybdenum, chromium, tungsten, vanadium, rhodium, copper, zinc, and combinations thereof and at least one promoter, said metal and promoter being dispersed on a support to form a catalyst particle. The preferred support is alumina. The particles have a BET surface area of from about 100 m²/g to about 250 m²/g, and the metal and promoter are dispersed on the support such that the crystallite size of the metal oxide is from about 40 Å to about 200 Å.

In certain reactions it may be beneficial to use cobalt deposited on a titania support rather than cobalt on alumina. For example, as reported by Oukaci et al (Applied Catalysis A: General 186 (1999) 129 – 144)), cobalt supported on titania is preferred by some workers for Fischer-Tropsch reactions because it is more active for CO hydrogenation than cobalt catalysts supported on alumina or silica or other supports. Furthermore titania supported catalyst may be preferred for use in acid reaction media where gamma alumina supports may show a tendency to dissolve to some extent.

US-A-5968991 describes a process for the preparation of a catalyst useful for conducting carbon monoxide hydrogenation reactions, especially a Fischer-Tropsch catalyst. In the preparation of the catalyst, a solution of a multi-functional carboxylic acid having from about 3 to 6 total carbon atoms, especially glutamic or citric acid, is employed to impregnate and disperse a compound or salt of rhenium and a compound or salt of a catalytic metal, or metals, e.g., copper or an Iron Group metal such as iron, cobalt, or nickel onto a refractory inorganic

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oxide support such as titania. This method of preparation requires repeated impregnations in order to achieve the desired cobalt loadings.

US-A-6130184 describes a process for the preparation of a cobalt-containing catalyst or catalyst precursor, comprising mixing titania or a titania precursor, a liquid, and a cobalt compound, which is at least partially insoluble in the amount of liquid used, to form a mixture, shaping and drying of the mixture thus-obtained, followed by calcination.

US-A-5545674 describes a process for preparing cobalt catalysts supported on titania spheres by spraying the hot titania spheres with an aqueous cobalt nitrate and perrenic acid mixture, optionally after soaking the support spheres in a non-aqueous liquid to provide a non-uniformly distributed cobalt catalyst.

US-A-4595703 describes a cobalt-titania catalyst, or thoria promoted cobalt-titania catalyst used in a Fischer-Tropsch process wherein cobalt, or cobalt and thoria, is composited, or dispersed upon titania, TiO_2 , or a titania-containing carrier, or support, wherein the support contains a rutile:anatase ratio of at least about 2:3, and preferably at least about 3:2.

In comparison with other catalytic metals such as copper and nickel used for hydrogenation reactions, cobalt is a relatively expensive and so, to obtain the optimum activity, it is desirable that as much as possible of the cobalt present is in an active form accessible to the reactants. It is therefore desirable to maximise the surface area of the cobalt in the supported catalysts. It is desirable to manufacture a cobalt catalyst supported upon titania which is useful in the Fischer-Tropsch process by depositing a relatively high loading of well-dispersed cobalt species upon the support.

Accordingly we now provide a process for manufacturing a catalyst which comprises a cobalt species on a solid titania support, comprising mixing together particles of a solid titania support and an aqueous solution of cobalt ammine carbonate, and heating to an elevated temperature sufficient to effect decomposition of the cobalt ammine carbonate and precipitation of cobalt compounds onto said support.

In one embodiment of the invention we provide a method of making a catalyst comprising a cobalt species on a titania support, comprising the steps of mixing a titania particulate material with an aqueous solution of a soluble cobalt compound, heating the mixture of particulate material and cobalt compound to effect precipitation of cobalt compounds on the titania, filtering the solid residue from the aqueous medium, and drying.

In a further embodiment of the invention we also provide a process for the production of a catalyst comprising saturating a titania catalyst support with an aqueous solution of cobalt ammine carbonate, and removing the excess of the solution, before

heating the resulting product to a temperature sufficient to effect decomposition of the cobalt ammine carbonate.

The solid residue comprising the catalyst may optionally be calcined and, optionally, reduced.

The term "cobalt species" is used broadly to include both elemental cobalt and cobalt in combined form, e.g. as compounds such as cobalt oxides and cobalt hydroxycarbonates. The cobalt compounds which are precipitated on the support as a result of heating the aqueous solution of soluble cobalt compound comprise basic cobalt carbonate species and / or cobalt oxides.

The catalyst is normally used in its reduced form, i.e. in which a major proportion of the cobalt species is reduced to metallic cobalt. The catalyst may, however, be provided as a precursor wherein the cobalt is present as one or more compounds, such as oxides or hydroxy carbonates, reducible to elemental cobalt. In this form, the material may be a catalyst precursor and may be treated to reduce the cobalt compounds to metallic cobalt. Alternatively the oxidic material may itself be useful as a catalyst and used as supplied, e.g. for oxidation reactions. The cobalt surface area figures used herein apply to the material after reduction, but the invention is not limited to the provision of reduced catalyst.

By the term total cobalt, we mean the amount of cobalt whether present in elemental or combined form. Generally however at least 70% by weight of the total cobalt in the reduced catalyst will be in the elemental state.

The catalysts of the invention preferably have a cobalt to titanium atomic ratios in the range 0.01 to 50, particularly 0.03 to 25 and especially 0.05 to 10.

The titania may be formed from natural sources or may be a synthetic, e.g. precipitated titania. The titania may be in the form of a powder or a shaped granular material, e.g. as extruded or tabletted titania pieces. In shaped forms, the support may additionally comprise forming aids such as a lubricant and/or binder. The titania may optionally comprise up to 20% by weight of another refractory oxide material, typically silica, alumina or zirconia. The titania may alternatively be present as a coating on a support which is preferably of silica or alumina, typically as a coating of 0.5 to 5 monolayers of titania upon the underlying support. Therefore when we refer to titania we include titania-coated supports.

Suitable powdered titanias typically have particles of surface weighted mean diameter $D[3,2]$ in the range 1 to 100 μm , particularly 3 to 100 μm . If desired, the particle size may be increased by slurring the titania in water and spray drying. Preferably the BET surface area of the particles is in the range 10 to 500 m^2/g . Conventional titania supports for F-T catalysts are

based upon rutile forms of titania, which has superior attrition resistance compared with anatase forms. These titanias are normally of relatively low surface area, e.g. about 10 – 100 m²/g. Higher surface area titania catalyst supports, having surface areas > 300 m²/g are now available commercially and these are very suitable for use in the present invention.

Granular titanias may have a variety of shapes and particle sizes, depending upon the mould or die used in their manufacture. For example the particles may have a cross-sectional shape which is circular, lobed or other shape and a length from about 1 to 10 mm. The surface area is generally in the range 10 – 500 m²/g, preferably 100 to 400 m²/g.

The pore volume of the titania is generally between about 0.1 and 4 ml/g, preferably 0.2 to 2 ml/g and the mean pore diameter is preferably in the range from 2 to about 30 nm.

The cobalt compound is most preferably a cobalt ammine complex which is formed in situ in aqueous solution by dissolving basic cobalt carbonate in a solution of ammonium carbonate in aqueous ammonium hydroxide, to give a product of the desired cobalt content. The cobalt ammine carbonate solution may be made by dissolving basic cobalt carbonate in an aqueous solution of ammonium carbonate or ammonium carbamate containing additional ammonium hydroxide. The relative amounts should be such that the pH of the solution is in the range 7.5 to 12, preferably 9 to 12. The solution preferably contains 0.1 to 2.5 moles of the cobalt complex per litre. As the concentration of cobalt increases, then generally the proportion of carbonate ions relative to hydroxide ions in the basic cobalt carbonate feed should be increased. Additional ammonium hydroxide solution may be added in order to provide a slurry of handleable viscosity when the support particles are mixed in. The cobalt ammine complex compound is then heated, e.g. to a temperature in the range 60 to 110°C, to cause the cobalt ammine complex to decompose with the evolution of ammonia and carbon dioxide and to deposit a cobalt compound on the surface, and in the pores, of the titania. This step is conveniently carried out when slurrying titania powders with the cobalt compound so that the slurry is then maintained at the elevated temperature for a period, hereinafter the ageing period. The solid material is then filtered from the aqueous medium, washed and dried. Using this form of the process of the invention, a catalyst having a high cobalt dispersion and a high cobalt loading, e.g. > 10% cobalt, (more preferably > 15% cobalt, by weight) may be prepared in a single deposition step.

The amount of cobalt in the catalyst may be varied by varying the relative amount of cobalt and support present in the reaction mixture and by controlling the concentration of the solution of cobalt compound.

Alternatively the cobalt compound is absorbed into the pore structure of the titania particle by impregnating titania particles with the solution of cobalt compound. The particles

may then conveniently be separated from the remaining solution and the ageing process may be carried out by heating them e.g. to a temperature above 100°C for the ageing period of at least 60 minutes, preferably at least 100 minutes to decompose the cobalt compound held within the particles to deposit cobalt species in the structure of the titania particle. The particle may be subjected to successive impregnations, e.g. by separating them from the impregnation solution and drying before a subsequent impregnation.

The solid material may then be calcined in air, e.g. at a temperature in the range 250 to 450°C, to decompose the cobalt compound to cobalt oxide. The resultant catalyst precursor may be then reduced, e.g. with hydrogen, at a temperature between 300 to 550°C, more preferably below about 500°C, e.g. 330 - 420°C. Upon reduction, most, if not all, of the cobalt oxide is reduced to metallic cobalt; the result is cobalt metal in a highly dispersed form, i.e. having a high cobalt surface area. Alternatively the cobalt compound may be directly reduced, i.e. without the need for a calcination step.

Preferably the amounts of titania and cobalt ammine carbonate employed are such that the cobalt to titanium atomic ratio is in the range 0.03 to 5. Irrespective of the cobalt content of the catalyst, the particle size of the catalyst is essentially the same as the particle size of the titania.

The catalysts of the invention preferably contain 3 to 75% by weight of total cobalt. When a low surface area form of titania is used, i.e. having a BET area of < 100 m²/g, then the cobalt content may more usually be below 40% by weight total cobalt, e.g. 5 – 35% by weight total cobalt. The amount of cobalt which is desirable varies according to the type of reaction for which the catalyst is used. Selection of an appropriate amount of cobalt is easily determined or known by the skilled person. Preferred catalysts typically have a cobalt surface area in the range 15 to 100, particularly 20 to 40 m² per gram total cobalt.

The cobalt surface area is determined by H₂ chemisorption. The sample (about 0.5 g) is degassed and dried under vacuum at 120°C and then reduced by heating to 425°C (unless specifically mentioned otherwise) at a rate of 3°C per minute whilst hydrogen gas is passed through the sample at a flow rate of 250 ml/min for 18 hours. The sample is then heated under vacuum to 450°C over 10 minutes and maintained under those conditions for 2 hours. Following this pre-treatment, the chemisorption analysis is carried out at 150°C using pure H₂ gas. The full isotherm is measured up to 800 mm Hg pressure of H₂ and the straight line portion of the chemisorption isotherm between 300 and 800 mm Hg is extrapolated to zero pressure to calculate the volume of the gas (V) which is chemisorbed by the sample. The metal surface area is then calculated from the following equation:

$$\text{Cobalt surface area} = (6.023 \times 10^{23} \times V \times \text{SF} \times A) / 22414$$

where V = uptake of H_2 in ml/g

SF = Stoichiometry factor (assumed 2 for H_2 chemisorption on Co)

A = area occupied by one atom of cobalt (assumed 0.0662 nm^2)

This method of calculating cobalt surface area is described in the Operators Manual for the Micromeritics ASAP 2000 Chemi System V 1.00, Appendix C, (Part no 200-42808-01, 18th January 1991)

For hydrogenation reactions, the active form of the cobalt is elemental cobalt although in the active catalyst only some, rather than all, of the cobalt is normally reduced to the elemental form. Hence a useful measure is the exposed surface area of elemental cobalt per g of total cobalt present. Except where expressly indicated, as used herein, total cobalt contents are expressed as parts by weight of cobalt (calculated as cobalt metal, whether the cobalt is actually present as the metal or is in a combined form, e.g. as cobalt oxides) per 100 parts by weight of the catalyst or precursor thereto.

Useful catalyst products are formed by the dried precipitated product, a calcined (oxidic) product or a reduced product, depending on the use for which the catalyst is made.

When a catalyst composition requires a step such as calcination and/or reduction to produce the active form of catalyst for the desired reaction, it may be referred to as a catalyst precursor.

In a non-reduced form the catalysts may be useful in oxidation reactions e.g. to oxidise organic compounds, for example as in the treatment of effluent containing organic material.

The catalyst compositions of the invention may optionally include one or more promoter metals. Suitable promoter metals include boron, cerium, chromium, copper, iridium, iron, lanthanum, manganese, molybdenum, palladium, platinum, rhenium, rhodium, ruthenium, strontium, tungsten, vanadium, zinc, sodium, potassium, rubidium, caesium, magnesium, titanium, zirconium, and other rare earth metals and combinations thereof. The selection of a promoter metal is dependent upon the desired use of the catalyst. A preferred promoter is rhenium which appears to promote the formation of high cobalt surface areas in the reduced catalyst.

The catalysts, in reduced form, may be used for hydrogenation reactions such as the hydrogenation of aromatic or olefinic compounds, e.g. waxes, nitro, nitrile or carbonyl compounds, e.g. the conversion of nitrobenzene to aniline or the conversion of fatty nitriles to amines or the hydrogenation of aldehydes to the corresponding alcohols. They may also be used for the hydrogenation of paraffin waxes to remove traces of unsaturation therein. They may also be useful in a wide range of other reactions, for example the Fischer-Tropsch

process, i.e. where hydrogen and carbon monoxide are reacted in the presence of the catalyst to form higher hydrocarbons. This may be part of an overall process for the conversion of natural gas to petroleum compounds wherein the hydrogen / carbon monoxide gas mixture is a synthesis gas formed by steam reforming natural gas.

The catalyst may be provided in the form of a concentrate of the catalyst particles dispersed in a suitable carrier medium, e.g. hardened soybean oil or a hydrocarbon wax. Preferably the amount of catalyst in said concentrate is such that the concentrate has a total cobalt content of 3 to 30%, preferably 5 to 15% by weight. The catalyst may alternatively be subjected to a process to form shaped pieces such as by granulation, tableting, extrusion or other known methods, optionally with the addition of processing aids such as lubricants or binders.

When the catalyst is to be used in a reduced form, it may be supplied in non-reduced form, i.e. as a catalyst precursor, to be reduced in-situ before use or alternatively the catalyst may be reduced and then passivated in order to protect the reduced metal during subsequent storage and transport. Methods of protecting the catalyst are well known.

The invention is illustrated by the following examples in which the stock solution employed was made up using 1707 g ammonia solution (SG 0.89, 30% ammonia), 198 g ammonium carbonate, 218 g basic cobalt carbonate (46.5% wt% Co, bulk density 0.640 g/ml) and 1877 g demineralised water. The total volume of the stock solution was 4 litres.

The carrier employed was P25 titania supplied by Degussa, having a surface area of 50.6 m²/g (as measured by BET methodology) and a pore volume (as determined by nitrogen porosimetry from the P/Po = 0.980 values of the desorption isotherm) of about 0.14 ml/g and having a mean diameter D[3,2] of 1.7 µm. The average pore diameter, calculated as $4 \cdot V_p / S_{BET}$, where V_p is the pore volume (m³/g) and S_{BET} is the BET surface area (m²/g), was about 11 nm. The phase ratio of this titania is about 83% anatase and 17% rutile.

Example 1.

A portion of the stock solution was diluted with 7 parts by volume of a 9 wt% ammonia solution per part by volume of the stock solution in order to reduce the viscosity of the slurry produced by mixing the solution with the carrier particles. The pH of the diluted stock solution was 11.1.

The titania carrier particles and an amount of the diluted stock solution corresponding to a nominal 5% by weight of cobalt, based on the weight of the titania particles, were charged to a stirred vessel equipped with a condenser for removal of liquid by distillation. The mixture was heated to boiling while stirring and gentle boiling at about 96°C was maintained for a

period of time. After about 90 min total heating time the solution became clear. After a total heating time of 130 min part of the mixture was filtered and the solid recovered, washed and then dried in air at 110°C overnight so give sample A.

The gentle boiling was continued for the remaining portion of the mixture for a further 20 min (to give a total heating time of 150 min) and then the mixture was filtered and the solid recovered, washed and then dried in air at 110°C overnight so give sample B.

The resultant catalyst precursors A and B were then reduced by passing hydrogen through a bed of the catalyst while heating to 425°C. The cobalt surface area was determined by H₂ chemisorption as described hereinbefore.

Example 2

Example 1 was repeated, but using undiluted stock solution and total heating times of 130 and 150 min. The amount of stock solution employed was such as to give a nominal 10% by weight of cobalt, based on the weight of the titania particles.

Example 3

Example 1 was repeated but using 1 part by volume of the 9 wt% ammonia solution per part by volume of the stock solution, and an amount of the diluted stock solution such as to give a nominal 15% by weight of cobalt, based on the weight of the titania particles. The total heating times were 120, 140 and 160 min.

Example 4

Example 2 was repeated, using undiluted stock solution in such an amount that the nominal cobalt content was 20% by weight based on the weight of the titania particles. The total heating times were 70, 95, 120 and 135 min.

Example 5

Example 1 was repeated but using 1 part by volume of the 9 wt% ammonia solution per part by volume of the stock solution, and an amount of the diluted stock solution such as to give a nominal 25% by weight of cobalt, based on the weight of the titania particles. The total heating times were 60, 80 and 100 min.

The cobalt content of the reduced catalyst was calculated from the measured cobalt content of the unreduced material and the weight difference between the unreduced material and the reduced catalyst. The chemisorption results are shown in Table 1.

A sample of the precursor, i.e. before reduction, of Example 4D was subjected to temperature programmed reduction in a 5% hydrogen in nitrogen gas stream. The sample was

first heated to 120 °C to remove moisture and thereafter from 120 to 1000 °C in the hydrogen stream at a heating rate of 5 °C per minute. The change in concentration of hydrogen between the inlet gas and the outlet gas was monitored by a katharometer to show the consumption of hydrogen at each temperature. The results showed peaks at 195°C, 275°C and 435°C. The 275°C peak probably is reduction of Co_3O_4 to CoO while the 435°C peak corresponds to reduction of CoO to the cobalt metal. There is no evidence for any species reducing at high temperatures suggesting that all cobalt may be reducible and that there is little unreducible cobalt titanate formation.

Table 1

Example	Heating time (min)	Cobalt content (% wt)		Cobalt surface area	
		Precursor before reduction	Reduced catalyst	m ² per g of reduced catalyst	m ² per g of cobalt
1A	130	5.5	5.8	1.0	17
1B	150	5.4	5.6	1.4	25
2A	130	10.1	11.0	2.5	23
2B	150	10.0	11.0	1.9	17
3A	120	15.9	17.8	4.1	23
3B	140	16.0	17.8	3.9	22
3C	160	16.0	17.8	3.8	21
4A	70	16.1	18.1	4.6	25
4B	95	20.8	24.2	4.0	17
4C	120	21.1	24.6	5.4	22
4D	135	21.1	24.6	5.1	21
5A	60	26.4	31.4	6.4	20
5B	80	27.4	32.7	4.1	13
5C	100	27.7	32.5	5.7	18

As a comparison, a catalyst comprising 20% Co on a gamma alumina support (Puralox™ HP14/150, available from Sasol), prepared by a similar method was subjected to temperature programmed reduction under the same conditions. The corresponding peaks occur at about 225, 295 and 600 °C respectively. Additionally a small, broad peak is present at 800 – 900 °C, indicating the presence of a difficulty reducible cobalt compound, which is believed to be cobalt aluminate. Thus the cobalt catalysts on a titania support are more readily reducible than the comparable catalyst on an alumina support.

Examples 6 – 10

Catalysts were made by the method described in Example 1, using the P25 titania support which had been calcined at 730 °C for 4 hours to increase the rutile phase content. The calcined support consisted of about 75% rutile and 25% anatase forms of titania. The stock solution was diluted, where necessary, with a 30% aqueous ammonia solution in order to ensure that the slurry was of a convenient viscosity, and the amount of titania and solution was adjusted to provide the required final cobalt content. The results are shown in Table 2.

Table 2

Example	Heating time (min)	Cobalt content (% wt)		Cobalt surface area	
		Precursor before reduction	Reduced catalyst	m ² per g of reduced catalyst	m ² per g of cobalt
6A	75	7.0	7.2	1.7	23.8
6B	90	7.1	7.4	2.0	27.0
6C	105	7.2	7.5	2.3	30.5
6D	120	7.1	7.5	2.0	26.7
6E	150	7.3	7.8	1.9	24.4
7A	75	10.1	10.8	2.3	21.2
7B	90	9.9	10.6	2.5	23.5
7C	105	9.8	10.2	2.3	22.5
7D	120	9.9	10.7	2.3	21.5
7E	150	9.6	10.2	1.9	18.7
8A	85	13.2	14.4	2.7	18.8
8B	100	13.8	15.1	2.9	19.2
8C	115	13.7	15.0	3.4	22.7
8D	130	13.6	15.0	2.6	17.4
8E	150	13.9	14.9	3.4	22.8
9A	90	21.6	25.1	3.6	14.3
9B	105	21.8	25.3	3.3	13.0
9C	120	21.9	25.7	3.8	14.8
9D	135	22.1	25.6	3.3	12.9
9E	150	21.4	24.6	4	16.3
10A	75	22.6	26.6	3.9	14.7
10B	90	22.4	26.0	3.2	12.3
10C	105	22.8	26.4	3.6	13.6
10D	120	22.3	25.9	3.5	13.5
10E	150	22.7	25.7	4.5	17.5

Example 11

A cobalt on titania catalyst containing 20% cobalt by weight, made according to Example 1, was impregnated with a 45% aqueous perrhenic acid solution by spraying the solution into a rotating drum containing the catalyst. The quantity of solution was calculated to give 1% rhenium by weight of catalyst. The surface area was measured using hydrogen chemisorption as described earlier and the results for the Re-promoted and un-promoted catalyst are shown in Table 3. The surface area was measured for a reduction temperature of 425 °C and also for a sample reduced at 350 °C. Temperature programmed reduction of the Re-containing catalyst showed the major cobalt oxide reduction peak maximum at about 400 °C compared with about 435 °C for the catalyst containing no rhenium.

Table 3

Example 11	% wt Re	Cobalt content (% wt)			Cobalt surface area			
					425 °C		350 °C	
		Precursor before reduction	Reduced catalyst (425 °C)	Reduced catalyst (350 °C)	(m ² g ⁻¹ cat)	(m ² g ⁻¹ Co)	(m ² g ⁻¹ cat)	(m ² g ⁻¹ Co)
unpromoted	---	19.5	22.9	21.7	4.8	20.9	7.2	33.2
Re doped	1.0	19.5	22.4	21.6	5.4	24.1	6.2	28.7

Example 12

The performance of the catalyst of Example 5C was tested in a Fischer Tropsch reaction.

The catalyst (10g) was first reduced in a fixed reactor at 400°C for 4 h using 700ml/min H₂. 7.6 g reduced catalyst was then transferred to a 1 litre CSTR and re-reduced in-situ at 230°C for 15hours using 5 Standard l/h/g cat of hydrogen before starting the Fischer-Tropsch reaction at 20 bar and 180°C while raising the temperature to 210°C in 3 hours. The flow of the gas mixture (molar ratio H₂ : CO 2.1 : 1) was then adjusted to reach approximately 50% conversion. At a space velocity of 5 Standard l/h/g cat H₂ and after 48.5 h, the following performance was observed - 51.4% conversion of CO, with the following selectivities to different products; 4.3% to CH₄, 0.3% to CO₂, 1.67% to C₂-C₄ olefins, 1.42% to C₂-C₄ paraffins and 92.31% to C₅+ organic compounds. As a comparison cobalt on alumina catalysts made by a similar process were tested under the same conditions and the selectivities are shown in Table 4.

Example 13

Catalysts were made using the method of the invention in which the support was a titania-coated alumina. The support was prepared by diluting 128g tetraisopropyl titanate (VERTEC™ TIPT) in 1000 g isopropanol and then mixing with 400g of a gamma alumina (Puralox™

HP14/150, available from Sasol) at 45 °C for 30 minutes in a rotary evaporator. The isopropanol is then removed by distillation and the temperature is increased to 90 °C and the pressure reduced to a vacuum. The resulting particles were calcined at 400 °C for 8 hours after drying at 120 °C for at least 15 hours. The support contained 5.4% Ti based on the weight of alumina. Samples 13 A and 13B were made using these supports using the method described in Example 1.

Table 4

	Example 5C	Comp A	Comp B
Co % (reduced catalyst)	27.7	32.8	19.3 + 1% Re
Support	titania	theta alumina	gamma alumina
CO conversion (%)	54	61	49
Sel (CH ₄)%	4.3	6.5	8.2
Sel (CO ₂) %	0.3	0.2	0.4
Sel (C ₂ – C ₄ olefin) %	1.7	4.5	3.9
Sel (C ₂ – C ₄ paraffin) %	1.4	6.0	6.5
Sel (C ₅ + organics) %	92.3	81.8	82.0

Example 14

400g of Puralox™ HP14/150 alumina was mixed with a solution of 138g of 76% aqueous titanium lactate diluted in 2500g of deionised water for 30 minutes. The resulting slurry was adjusted to pH 9.5 using 192 g of 14% ammonia solution. The solids were then removed by vacuum filtration, re-slurried in water and washed twice in 2 litres of deionised water. The resulting particles were calcined at 400 °C for 8 hours after drying at 120 °C for at least 15 hours. The support contained 5.4% Ti based on the weight of alumina. The support was then used to prepare catalysts 14 A and 14B by the method described in Example 1. The cobalt surface areas were determined by H₂ chemisorption as described above and the results are shown in Table 5.

Table 5

Example	Heating time (min)	Cobalt content (% wt)		Cobalt surface area	
		Precursor before reduction	Reduced catalyst	m ² per g of reduced catalyst	m ² per g of cobalt
13A	110	14.6	16.5	12.3	74.4
13B	110	29.6	38.0	21.1	55.5
14A	110	15.5	17.6	12.2	69.3
14B	110	30.7	41.0	21.8	53.5

Claims.

1. A process for manufacturing a catalyst which comprises a cobalt species on a titania support, comprising mixing together said titania support and an aqueous solution of cobalt ammine carbonate, and heating to an elevated temperature sufficient to effect decomposition of the cobalt ammine carbonate and precipitation of an insoluble cobalt compound onto said titania support.
2. A process as claimed in claim 1, comprising saturating a titania support with an aqueous solution of cobalt ammine carbonate, and removing the excess of the solution, before heating the resulting product to a temperature sufficient to effect decomposition of the cobalt ammine carbonate.
3. A process as claimed in claim 1, wherein the mixture of titania support and said cobalt solution is heated to a temperature sufficient to effect decomposition of the cobalt ammine carbonate in situ before separating the solid catalyst from the mixture and drying.
4. A process as claimed in any of claims 1 to 3, wherein the titania support and cobalt solution are maintained at an elevated temperature for a period of at least 60 minutes.
5. A process as claimed in any of claims 1 to 4, wherein said temperature is in the range 60 to 110°C.
6. A process as claimed in any of claims 1 to 5, further comprising the step of calcining the resulting catalyst product at a temperature between 200 and 600°C.
7. A process as claimed in any of claims 1 to 6 further comprising the step of reducing the resulting catalyst product with hydrogen at a temperature between 300 to 550°C.
8. A process as claimed in claim 7, further comprising the step of dispersing the reduced catalyst in particulate form product in a carrier matrix.

9. A process as claimed in any one of claims 1 to 9, wherein the pH of the mixture of titania particles and aqueous cobalt ammine carbonate complex is maintained above 7.5 during the heating step.
10. A catalyst or catalyst precursor made by the process claimed in any of claims 1 to 9.
11. A process for the hydrogenation of an organic compound comprising an olefinic, carbonyl, nitrile, nitro or aromatic group, comprising reacting said compound with hydrogen in the presence of a catalyst as claimed in claim 10.
12. A process for the formation of a hydrocarbon by the reaction of carbon monoxide with hydrogen in the presence of a catalyst as claimed in claim 10.
13. A process as claimed in claim 11 or claim 12 further comprising the step of forming an active catalyst in situ by reducing a catalyst precursor as claimed in claim 10 with hydrogen before conducting said hydrogenation reaction.
14. A process for the oxidation of an organic compound by reaction with an oxygen-containing compound in the presence of a catalyst as claimed in claim 10.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB03/04109

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J23/75 B01J37/03 C10G2/00 C07C1/04 C07C29/132
C07C209/36 C07C209/48 C07C5/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C10G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	OUKACI R ET AL: "Comparison of patented Co F-T catalysts using fixed-bed and slurry bubble column reactors" APPLIED CATALYSIS A: GENERAL, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 186, no. 1-2, 4 October 1999 (1999-10-04), pages 129-144, XP004271930 ISSN: 0926-860X cited in the application tables 1,5-8	10,12,13
X	EP 0 266 898 A (EXXON RESEARCH ENGINEERING CO) 11 May 1988 (1988-05-11)	10,12,13
Y	the whole document	1-9
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB98/04109

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 926 235 A (CHEMETRON CORP) 15 May 1963 (1963-05-15) the whole document ---	1-9
P,X	WO 02 089978 A (SUD CHEMIE INC) 14 November 2002 (2002-11-14) cited in the application claims 1,8,11,12,15-17,26 page 9, line 4 - line 9 page 16, line 13 - line 15 ---	1-8,10, 12,13
P,X	WO 03 024905 A (CONOCO INC) 27 March 2003 (2003-03-27) claims 1,5,6,8,9,11-13,23,29,39,51,52 page 4, line 22 -page 5, line 17 ---	1-8,10, 12,13
X	EP 1 163 955 A (KATALEUNA GMBH CATALYSTS) 19 December 2001 (2001-12-19) claim 1 paragraph '0001! ---	10,11
X	WO 98 47617 A (EXXON RESEARCH ENGINEERING CO) 29 October 1998 (1998-10-29) claims 1-10 table 1 ---	10,12,13
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 577 (C-1122), 20 October 1993 (1993-10-20) & JP 05 168932 A (NKK CORP), 2 July 1993 (1993-07-02) abstract ---	10,14
A	WO 01 62381 A (LOK MARTIN CORNELIS ;ICI PLC (GB); BAILEY STEPHEN (GB); GRAY GAVIN) 30 August 2001 (2001-08-30) the whole document -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Publication No

PCT/GB/04109

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0266898	A	11-05-1988	AU 623756 B2	21-05-1992
			AU 5220890 A	03-10-1991
			AU 589806 B2	19-10-1989
			AU 7930687 A	14-04-1988
			CA 1312066 C	29-12-1992
			CA 2012682 A1	21-09-1991
			DE 3750154 D1	04-08-1994
			DE 3750154 T2	20-10-1994
			EP 0266898 A2	11-05-1988
			EP 0453674 A1	30-10-1991
			JP 2572079 B2	16-01-1997
			JP 63147545 A	20-06-1988
			NO 874162 A ,B,	05-04-1988
			US RE37406 E1	09-10-2001
			US 4962078 A	09-10-1990
			US 4977126 A	11-12-1990
			US 5545674 A	13-08-1996
			US 5128377 A	07-07-1992
			US 6319960 B1	20-11-2001
GB 926235	A	15-05-1963	FR 1268260 A	28-07-1961
WO 02089978	A	14-11-2002	WO 02089978 A1	14-11-2002
WO 03024905	A	27-03-2003	WO 03024905 A1	27-03-2003
			US 2003105170 A1	05-06-2003
EP 1163955	A	19-12-2001	DE 10059319 A1	28-02-2002
			EP 1163955 A1	19-12-2001
WO 9847617	A	29-10-1998	US 5856260 A	05-01-1999
			AU 744172 B2	14-02-2002
			AU 7136798 A	13-11-1998
			EP 0977629 A1	09-02-2000
			JP 2001522300 T	13-11-2001
			NO 995138 A	30-11-1999
			TW 491731 B	21-06-2002
			WO 9847617 A1	29-10-1998
			US 6331575 B1	18-12-2001
JP 05168932	A	02-07-1993	JP 2697441 B2	14-01-1998
WO 0162381	A	30-08-2001	AU 3213401 A	03-09-2001
			EP 1257358 A1	20-11-2002
			WO 0162381 A1	30-08-2001
			US 2003032684 A1	13-02-2003